Review

Direct visualization of lithium via annular bright field scanning transmission electron microscopy: a review

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Abstract

Annular bright field (ABF) scanning transmission electron microscopy has proven able to directly image lithium columns within crystalline environments, offering much insight into the structure and properties of lithium-ion battery materials. We summarize the image formation mechanisms underpinning ABF imaging, review the experimental application of this technique to imaging lithium in materials and overview the conditions that help maximize the visibility of lithium columns.

Key words: scanning transmission electron microscopy, atomic-resolution imaging, annular bright field, lithium, detector geometry, image simulation

Introduction

Rechargeable lithium batteries are now a mainstay for powering mobile electronic devices [1–5] and a promising prospect for electrochemical energy storage in hybrid electric vehicles and renewable energy plants [2–5]. Their attractive properties, such as high energy density and design flexibility, largely derive from the intrinsic properties of the electrode materials used. Ongoing efforts seek to refine existing designs and find new materials that may offer still more favorable compromises between factors such as energy density, power output, capacity, lifespan, cost, safety, toxicity and range of operational temperature.

The ability to directly observe at the atomic scale the structure of candidate electrode materials and the changes they undergo during the charging/discharging (lithiation/delithiation) cycle can offer important insights.

Transmission electron microscopy (TEM) is a powerful tool for structure determination of materials at high resolution. Frequently touted strengths of electron imaging relative to X-ray or neutron imaging include the strong interaction of electrons with materials, thus encoding rich information about the samples through which they scatter, and the relative ease with which electrons can be focused by magnetic lenses, thus providing information with high...
spatial resolution. However, the strength of interaction between fast electrons and atoms scales with the atomic number, making low-atomic-number lithium challenging to image, especially in the presence of heavier and therefore more strongly scattering elements. Nevertheless, in 2003 Shao-Horn et al. [6] demonstrated atomic-resolution imaging of lithium in LiCoO$_2$ in high-resolution TEM data processed via exit-surface wave reconstruction, a numerical method to determine the wavefield from multiple intensity images and thereby correct for aberrations in the electron lens. The development of aberration correctors [7,8] has since made atomic-resolution TEM imaging more routine and improved the quality of such exit-surface wave reconstructions [9].

However, for direct imaging of lithium at atomic resolution, scanning transmission electron microscopy (STEM) has recently proven particularly popular [10–42]. In aberration-corrected STEM, an atomically fine electron probe is raster scanned across a sample and images built up by plotting the signals recorded on various detectors as a function of probe position. Different detector geometries give different imaging modes. Using an annular detector with inner angle much larger than the probe-forming aperture convergence angle – schematic on the left in Fig. 1 – leads to so-called high-angle annular dark field (HAADF) imaging. Its success arises from the direct visual interpretability of the images and their robustness to sample thickness. However, the intensity of atomic columns in HAADF-STEM images scales approximately as the square of their atomic number, making it exceedingly difficult (though not impossible [13]) to image lithium columns when neighboring heavy-element columns are present. Figure 1 includes an example HAADF image of LiCoO$_2$ viewed along the [0 1 0] zone axis. The heavy Co columns are clearly visible as bright peaks, but the light O columns are barely visible and the Li columns are not visible. Direct, atomic-resolution STEM imaging of lithium is instead predominantly achieved via so-called annular bright field (ABF) imaging [43–45], which uses an annular detector with outer angle commensurate with the probe-forming aperture convergence angle – schematic on the left in Fig. 1 – and has proven to allow for the simultaneous imaging of both light and heavy-element columns. Figure 1 also includes an example ABF image of LiCoO$_2$ viewed along the [0 1 0] zone axis. In the ABF image, the columns appear as dark troughs, but now the Co, O and Li columns are all clearly visible. (The idea of using an annular detector in the bright field goes back a long way [46–49]. However, the more recent appreciation that the scattering of atomically fine electron probes along columns leads to robust qualitative trends in the scattering distribution has renewed interest in this approach.)

Direct visualization of lithium via ABF remains challenging. It can fail if the lithium columns are too close to neighboring heavy-element columns, or if the space between lithium atoms along the column is large, or if the probe is not sufficiently fine [50]. Partly in consequence of this and partly for the complementary information provided, ABF imaging is often used in conjunction with other imaging modes, most notably HAADF imaging but also selected area electron diffraction [28,29,36,42] and electron energy loss spectroscopy [13,28,30,37,39,41]. The complementary use of different STEM imaging modes has been the focus of recent review articles [51,52]. This review will concentrate instead on the principles of ABF imaging, and the scope for refinement of this and closely related imaging modes.

**Conceptual overview of image formation mechanisms in ABF**

Figure 2 shows a conceptual schematic of STEM probe evolution through an on-axis, crystalline sample for three generic probe positions: (a) between columns, (b) on a column of light elements and (c) on a column of heavy elements. When the probe is positioned between columns, Fig. 2a, the scattering is such that the diffraction pattern intensity distribution is not greatly different to what it would be in the absence of a specimen – uniform intensity in the so-called bright field disk (within the cone of incident illumination) and little intensity in the so-called dark field (outside of the cone of incident illumination). When the probe is positioned on a column of light elements, Fig. 2b, the scattering redistributes some electrons into the dark field, but also peaks up the electron density in the center of the bright field. Because the total flux of electrons in
the diffraction plane is the same for all probe positions, both these effects come at the expense of a reduction of the electron density in the outer area of the bright field. The signal on the ABF detector, one which spans the outer portion of the bright field, thus decreases – this is the mechanism for absorptive-like contrast on a column of light elements [44,45]. When the probe is positioned on a column of heavy elements, Fig. 2c, the strong scattering leads to a much larger portion of electrons scattered out into the dark field, with a corresponding reduction of electron density throughout the bright field. The signal on the ABF detector is thus again decreased – this is the mechanism for absorptive-like contrast on a column of heavy elements [45].

The schematic in Fig. 2 constitutes a considerable simplification of the complex electron scattering that takes place as an atomically fine probe traverses a sample. In particular, the intensity distribution with the probe between columns tends to be quite complex, ‘uniform’ only on broad average. The formalism for describing probe ‘channeling’, i.e. scattering along atom columns (Fig. 2b and c, cf. geometrically spreading in Fig. 2a), is the so-called S-state channeling model [53]. The interference of these S-states – eigenstates transversely bound to the column – with the largely unscattered remaining states leads consistently to net constructive interference in the central portion and net destructive interference in the outer portion of the bright field [44]. Though the detailed location of interference maxima and minima varies with thickness, the schematic in Fig. 2 nevertheless highlights the qualitative tendency: light columns and heavy columns consistently reduce the intensity in the outer area of the bright field, giving directly interpretable images in which both light and heavy atom columns are simultaneously visible. Further discussion on image formation and dynamics in ABF imaging can be found in Refs [44,45].

For relatively light elements like oxygen and nitrogen, ABF imaging is quite robust over a wider range of structures and sample thicknesses. However, for lithium and
other extremely light elements, the attractive potential of the column is not always sufficient to provide the lateral binding force needed to maintain significant electron density along the column (compare the evolution of the wavefield within the sample in Fig. 2b with that in Fig. 2a). Consequently, the visibility of lithium in ABF imaging is more contingent on the crystal structure, sample thickness and imaging conditions. We return to the question of the most favorable conditions for direct lithium imaging via ABF in later, but to underscore that ABF imaging of lithium is quite tractable we first present an overview of experimental work making use of direct ABF imaging of lithium.

**Applications**

Following the first proof-of-principle demonstrations that direct imaging of lithium atomic columns in crystalline environments via ABF was possible [10–13,15], the technique rapidly joined the high-resolution TEM toolkit for materials science problems, overwhelmingly in the context of lithium-ion battery materials. In a number of studies exploring the structure and dynamics of lithium-bearing materials [16,21,23,30–33,35–40,42], ABF imaging gives just a piece of a larger story, which might involve selected area diffraction, HAADF imaging and/or electron energy loss spectroscopy. However, in a number of studies [14,19,20,22,26–29], direct ABF imaging of lithium plays the central role in observing the structure or structure changes of scientific and technological interest.

Direct imaging of lithium via ABF can be used simply to confirm the material structure and the locations of lithium within it. The experimental data in Fig. 1 is one such example, showing clearly the location of lithium within LiCoO$_2$. Such direct imaging has been used to confirm the lithium storage sites in TiNb$_2$O$_7$ [16], and observe the presence and intergrowth of rhombohedral LiTMO$_2$ (where TM = Ni, Co and Mn) and monoclinic Li$_2$MnO$_3$-like structures in Li$_{1.2}$Mn$_{0.567}$Ni$_{0.166}$Co$_{0.067}$O$_2$ [29]. In a more complex example, the red arrow in Fig. 3f shows the site occupancy of lithium in a lithium-poor lanthanum lithium titanate structure [28]. (ABF also conveniently images the oxygen columns, enabling clear observation of the tilting of the oxygen octahedron in Fig. 3h.)

For reversibility, lithium-ion cathodes tend to have an intercalation-type structure, where the host matrix should be essentially unchanged as lithium is added or removed [2]. Another use of ABF imaging is to observe changes in structure resulting from the delithiation process. Figure 4 shows ABF images of LiFePO$_4$ viewed along the [0 0 1] orientation in both pristine and delithiated states, and, as hoped, the host matrix structure is little changed. Except in the thinnest of specimens [18], there is no reliable relationship between the depth of the ABF trough and the number of lithium atoms present: visualization only distinguishes lithium presence from lithium absence. Nevertheless, samples can be prepared at different points in the charging/discharging cycle. In this way, Gu et al. [14] identify a staging phenomenon, whereby the partial delithiation takes place in alternative layers, and Lu et al. [20] show that lithium ions can change sites on lithiation/delithiation, with lithium ions occupying different sites in Li$_4$Ti$_5$O$_12$ and Li$_7$Ti$_3$O$_12$.

In some cases, it is possible to identify the coexistence of different phases within single ABF images. Figure 5 shows a phase interface in Li$_{1.4}$Rh$_2$O$_4$ that is clearly visible in the ABF image, Fig. 5a, but extremely difficult to identify in the simultaneously acquired HAADF image, Fig. 5b. Suo et al. [22] identify an ordered interface with staging structure between LiFePO$_4$ and FePO$_4$ phases in partially delithiated LiFePO$_4$. Sun et al. [26] show a three-phase mechanism by which Li$_4$Ti$_5$O$_12$ can store sodium ions, in part through direct imaging of a three-phase coexistence region.

Sometimes delithiation does induce appreciable changes in the host matrix. Lu et al. [23] report distortion of and spacing changes between the cobalt planes in LiCoO$_2$

![Fig. 3. Simultaneously acquired HAADF (upper) and ABF (lower) images of Li-poor La$_{2.3}$Li$_{0.7}$TiO$_2$ viewed along the (a–c) [1 0 0]P and (d–f) [1 1 0]P zone axes, with structure model (omitting the lithium atoms) overlaid. (a), (d) La-rich La2 columns; (b), (e) a single La-poor La2 column (arrowed) and (c), (f) adjacent La-poor La2 columns (arrowed). The ABF images show (red arrow in (f)) that lithium sits on an O$_4$ square window site. (g), (h) Magnified views of the regions indicated by large arrows in (a) and (c), respectively, with dashed lines highlighting the subtle tilting of O–Ti–O linkages in the latter, with a shifted titanium atom in (h) indicated by a black arrow. Reprinted with permission from Ref. [28]. Copyright (2013) American Chemical Society.](https://academic.oup.com/jmicro/article-abstract/66/1/3/2608002)
upon delithiation. Ma et al. [35] demonstrate distortion of MoO$_6$ octahedra during lithiation/delithiation. Substantial and non-reversible structure changes are implicated in capacity loss or capacity fading, the degradation of lithium-ion battery performance over many charge/discharge (lithiation/delithiation) cycles by changes in crystallinity that impede lithium diffusion. One established mechanism for this is the migration of transition metal ions into the lithium channels. Wang et al. [27] observe manganese migration into the lithium layer in Li$_2$MnO$_3$ after delithiation: upon charging, darker ABF contrast appears in lithium planes than can be accounted for by either lithium or oxygen atoms and which is therefore interpreted to be due to manganese occupancy, though the process is reversible upon discharging. Ultimately, tracking the motion of transition metal elements is better done by HAADF than ABF, and it is through that technique that irreversible behavior has been explored in detail [54]. Honma et al. [31,38] use a combination of ABF and HAADF to identify Li/Co antisite defects in LiCoPO$_4$, through contrast variation of nominal lithium columns, which similarly impacts the material’s electrochemical performance.

Structural changes at surfaces – the scope for which are enhanced by the possibility of chemical reaction with the surrounding electrolyte – significantly affect battery performance, since lithium must pass through the surface during cycling. Figure 6 shows an example of simultaneous HAADF and ABF images of a Li(Mn,Ni)$_2$O$_4$ surface, with arrows showing the strong contrast (bright for HAADF and dark for ABF) at the sites which in pristine Li(Mn, Ni)$_2$O$_4$ would be lithium columns but which are deduced to contain manganese/nickel atoms since these are the only strongly scattering elements present. The detailed surface structure in this system has been explored, primarily by HAADF but again with ABF data in support, in Ref. [55]. Antisite defects at surfaces after discharging have also been observed via ABF and HAADF in LiCoO$_2$ [23].

In the examples above, delithiation is not done in situ. Rather, a sequence of samples at different stages in the charging/discharging process is prepared. However, it is possible to use the electron beam irradiation to displace lithium atoms and so induce structural changes, which may
potentially occur in lithium-ion battery materials. Studies in the literature include LiV$_2$O$_4$ [19] and Li$_2$MnO$_3$ [37].

**Optimum imaging**

The experimental efforts described above rely primarily only on general ‘rules-of-thumb’ for ABF imaging: the probe must be atomically fine and the detector should approximately span the angular scattering range $\alpha/2 - \alpha$, where $\alpha$ is the probe-forming aperture angle. Nevertheless, because the ABF imaging of lithium is less robust than that of heavier elements, it is worth reviewing the conditions most favorable to ABF imaging of lithium [17,50].

As mentioned earlier, the formalism for describing probe channeling along atom columns (Fig. 2b,c, cf. geometrically spreading in Fig. 2a) is the so-called S-state channeling model. A STEM probe formed with a disk-like probe-forming aperture cannot couple perfectly to a column. However, having a larger fraction of the electron density coupling to the transverse bound state, the S-state, of the column usually improves the ABF contrast. The first corollary is that optimum ABF imaging occurs with the probe focused at the specimen entrance surface.

Considerations regarding probe coupling to the column S-state also influence the choice of accelerating voltage and probe-forming aperture cut-off. Figure 7 plots the fraction of electron density coupling to an isolated lithium column (assuming an along-column interatomic spacing of 2.84 Å, the value in LiCoO$_2$ viewed along the [0 1 0] zone axis) as a function of accelerating voltage and probe-forming aperture cut-off ($\alpha = \alpha/\lambda$, where $\alpha$ denotes the probe-forming aperture semi-angle and $\lambda$ denotes the relativistically corrected electron wavelength), with the mrad equivalent at 200 kV shown on the right hand axis.

To see how these considerations affect image appearance, Fig. 8 shows a mosaic of ABF images of LiCoO$_2$ viewed along the [0 1 0] zone axis as a function of accelerating voltage and probe-forming aperture angle. As per the predictions of Fig. 7, the lithium column visibility is seen to increase slightly at higher accelerating voltages. Similarly, the lithium column visibility is best at intermediate aperture cut-offs: at high aperture cut-offs the visibility...
of all columns is reduced, whereas at low aperture cut-offs, the interpretability reduces as the probe becomes wide enough to overlap multiple columns simultaneously.

It may sometimes be possible to improve the visibility of lithium columns by judicious choice of detector inner and outer angles \[50,57\]. However, the optimum conditions depend not only on the specimen structure but also on the specimen thickness. Until pixel detectors allowing for post-acquisition synthesis of arbitrary detector configurations become fast enough for routine use in STEM \[58–61\], we cannot offer any general advance on the standard rule-of-thumb that the ABF detector should span the range \(\alpha/2 - \alpha\).

Though not meaningfully a variable for any particular materials science problem, it is worth emphasizing that the visibility of lithium columns in ABF imaging depends on the structure of the material. Lithium is expected to be more visible if the along-column interatomic spacing between lithium atoms is smaller, since this makes the S-state more narrow and so optimum coupling occurs for finer probes. It also helps if the between-column spacing is large, as the coupling model breaks down when adjacent columns are very close together. This is demonstrated in Fig. 9, which presents ABF simulations of four different lithium-bearing materials with different along-column interatomic spacing between the lithium atoms. The lithium columns are most clearly visible in LiCoO2 viewed along the \([0 1 0]\) direction, where the along-column spacing between lithium atoms is just 2.8 Å. They become gradually fainter in LiNbO3 viewed along the \([220\bar{1}]\) zone axis (along-column spacing 3.8 Å), LiFePO4 viewed along the \([0 0 1]\) zone axis (along-column spacing 4.69 Å) and LiMn2O4 viewed along the \([1 1 0]\) zone axis (along-column spacing 5.8 Å). Note that these simulations include neither spatial incoherence nor scan and shot noise, both of which make lithium columns still harder to observe in experiments.

All the discussion above assumes the image formation mechanism is dominated by channeling contrast, which holds for samples of thickness upwards of 5–10 nm or so.

**Fig. 8.** Tableaux of simulated ABF images of LiCoO2 viewed along the \([0 1 0]\) zone axis for various accelerating voltages and probe-forming aperture cut-offs and assuming a 100 Å thick sample. In each case, the ABF detector is assumed to span the angular range \(\alpha/2 - \alpha\).

**Fig. 9.** Simulated ABF images of various Li-bearing materials with different along-column interatomic distances between lithium atoms, \(d_{ij}\), assuming 100 Å thick samples, 300 keV electrons, a 20 mrad probe-forming aperture semi-angle and an ABF detector spanning the range 10–20 mrad.
For thinner samples, bright field imaging can be better understood in terms of phase contrast. Consequently, contrast reversals are possible depending on the aberrations present in the probe-forming lens [25,62]. While from an experimental perspective this potential for ambiguity is often undesirable, it can be used to advantage. Lee et al. [18] show that in very thin crystals it is possible to count the number of lithium atoms in a column based on the ABF intensity – a summary of their analysis is shown in Fig. 10. For thicker crystals, where channeling contrast dominates, the ABF intensity does not vary monotonically with (indeed is largely insensitive to) the number of lithium atoms along the column and atom counting via ABF is not generally possible.

**Variant approaches**

Discussion of the schematics in Fig. 2 focused on the reduced intensity in the outer area of the bright field as the mechanism for absorptive-type contrast in ABF images. However, all incident electrons must go somewhere and Fig. 2b shows that when the probe is situated on a light-element column the reduction in intensity in the outer area of the bright field disk is accompanied by a corresponding increase in intensity in both the center of the bright field and in the low-angle dark field. This was recognized by Ohtsuka et al. [63] who showed that in middle angle bright field (MABF) images – the signal obtained on a disk detector spanning the central portion of the bright field – light elements appear with bright contrast. Despite the smaller span of the MABF detector relative to the ABF detector, it is nevertheless larger than the point on-axis detector which would give STEM contrast identical, by reciprocity, to conventional TEM [64]. Consequently, as Ohtsuka et al. [63] showed, MABF contrast for light elements is not plagued by the thickness-dependent contrast reversal problems of conventional TEM. That said, MABF contrast has a complex sensitivity to element weight. As per Fig. 2c, when the probe is situated on a heavy-element column the reduction in intensity throughout the bright field disk due to thermal scattering means that in MABF heavy elements appear with dark contrast. This juxtaposition of bright contrast for light elements and dark contrast for heavy elements can enhance the resolvability of and discrimination between the different sorts of column [63]. However, intermediate-weight-element columns are therefore problematic, appearing bright in thin crystals, where the elastic scattering forward focusing dominates while thermal scattering is small, but changing to dark contrast with increasing thickness as thermal scattering starts to dominate. Kotaka [24] showed that this qualitative ambiguity can be overcome by combining information from MABF images with that from HAADF images: color composite images formed using HAADF and MABF images allow for clear visualization of the structure and easy distinction between different elemental-weight columns, including example experimental data for LiCoO$_2$.

Simulated ABF, MABF and a color composite HAADF/MABF images for LiFePO$_4$ viewed along the [0 0 1] zone axis are shown in Fig. 11. In particular, the color...
composite gives a strong visual sense not only of the column locations but of their different scattering strengths, with the strongly scattering Fe columns appearing yellow, and the successively more weakly scattering P/O, O and Li columns appearing increasingly red.

Findlay et al. [65] further showed that if ABF and MABF images can be simultaneously recorded on the same scale, their difference yields an enhanced ABF (eABF) image in which the signal-to-noise ratio and the visibility (relative to heavier columns) of light-element columns are increased. Simulations for eABF are shown in Fig. 11, and the lithium columns are notably more visible in this mode than in standard ABF. To the best of our knowledge, neither MABF nor eABF has yet been applied to materials science problems. However, developments in segmented detectors [66] and pixel detectors [58–61] should make such imaging modes more widely available.

ABF, MABF and eABF are primarily qualitative imaging modes. Geared toward visual identification of the presence and location of light-element columns, their robustness (which, as discussed earlier, has limits for very light elements like lithium) is taken as license to make deductions about the structure with relatively little prior knowledge: STEM as a tool for discovery. For such purposes, signal-to-noise is a natural metric. However, for maximum sensitivity at low dose or for precision refinement, alternative metrics are possible. Gonnissen et al. [57] use statistical detection theory to determine annular detector inner and outer angles to minimize the probability of error on identifying whether a light-element column is present. Their analysis, including application to simulated data for LiV$_2$O$_4$, shows that ABF is not always the most optimal method, low-angle ADF often being competitive, perhaps because of the higher signal-to-background ratio. One route to such optimum detector geometries may come through current rapid developments in high-speed pixel detectors [58–61], which will offer the freedom to synthesize particularly favorable detector geometries in post-processing. While the technology and data handling for high-speed pixel detectors are still under development, it seems likely that we shall see their application to materials science problems in the next few years, particularly to beam-sensitive materials where dose efficiency is critical.

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